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Note

Comparison of gas–solid chromatography properties of tris(ethylenediamine)chromium(III) cation-exchanged montmorillonite, hectorite and attapulgite

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Recently, we described[1] the use of tris(ethylenediamine) complexes of Co(III), Cr(III) and Cu(II) exchanged onto montmorillonite as column packing materials for gas–solid chromatography (GSC). The most detailed study was carried out on the $Cr(en)_3^{3+}$-exchanged montmorillonite because of the intermediate d_{001}-spacing and surface area of $Cr(en)_3^{3+}$-montmorillonite and also because of its greater thermal stability.

Others have reported considerable differences in the gas chromatographic behaviour of dimethyldioctadecylammonium exchanged on various types of clays[2,3]. It was therefore thought that a study of some other clays exchanged with the $Cr(en)_3^{3+}$ cation might yield some interesting and useful results. Two clays, hectorite and attapulgite were chosen. Hectorite, a member of the smectite group, as is montmorillonite, is different in that it is trioctahedral (Mg^{2+}) rather than dioctahedral (Al^{3+}) in the octahedral layer of the structure. Attapulgite has a completely different crystal structure than the smectites, being more of a linear crystal than a platey crystal as are the smectites.

EXPERIMENTAL

Preparation of the 100% exchanged $Cr(en)_3^{3+}$-hectorite produced a material suitable for GSC studies. X-Ray diffraction indicated a d_{001}-spacing of 13.6 Å which was only slightly larger than the 13.4 Å found for the 100% exchanged $Cr(en)^{3+}$-montmorillonite. Comparative retention times obtained at 50° and a flow-rate of 120 ml/min are given in Table I.

TABLE I

RETENTION TIMES OF THE PACKINGS STUDIED

Values are in mm from point of injection using a chart speed of 25.4 mm/min.

	Air	CH_4	C_2H_6	N_2O
$Cr(en)_3^{3+}$-montmorillonite	4	7	67	120
$Cr(en)_3^{3+}$-hectorite	5	10	89	167

The retention time for air, methane and ethane is related to the d_{001}-spacing. The retention is therefore slightly larger for the $Cr(en)_3^{3+}$-hectorite (13.6 Å) as one would predict. This is consistent with the retention time of 181 mm for ethane found when using $Co(en)_3^{3+}$-montmorillonite which has a d_{001}-spacing of 14.0 Å.

The N_2O retention time which on previously investigated clays was directly related to the surface area is again confirmed on this clay. The $Cr(en)_3^{3+}$-montmorillonite had a surface area of 215 m^2/g while the $Cr(en)_3^{3+}$-hectorite had a value of 305 m^2/g.

Although the initial retention times for ethane and N_2O on the $Cr(en)_3^{3+}$-hectorite and $Cr(en)_3^{3+}$-montmorillonite were somewhat different, the changes in retertion times upon heating follow an almost identical pattern. These changes are shown in Fig. 1 for $Cr(en)_3^{3+}$-montmorillonite and in Fig. 2 for the $Cr(en)_3^{3+}$-hectorite. The reader is referred to the explanation given in previously published work for the changes in retention times.

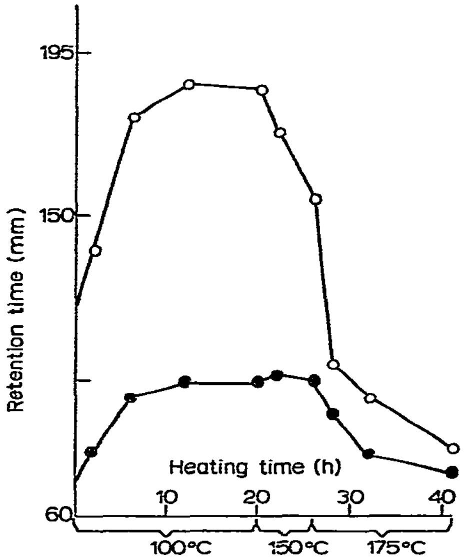

Fig. 1. Retention time *versus* heating time of (○) N_2O at 50° and 120 ml/min, and (●) C_2H_6 at 50° and 120 ml/min obtained on a 110-cm column of 100% $Cr(en)_3^{3+}$-montmorillonite.

GSC separation of methane, ethane, ethane, propane, *n*-butane and 2-pentene carried out on a 20-cm column of 100% $Cr(en)_3^{3+}$-hectorite gave near baseline separation. The analysis was carried out at 125° and a flow-rate of 120 ml/min. The result was graphically similar to that given previously[1] for the 75% $Cr(en)_3^{3+}$-montmorillonite.

Another exchanged clay prepared for comparison to the 100% $Cr(en)_3^{3+}$-montmorillonite was the comparable attapulgite. GSC data were impossible to obtain due to the high fragility of the clay. In attempting to grind and sieve the attapulgite clay for packing material it was found that almost all the clay became pulverized. This occurred even with rather mild grinding conditions. It is therefore evident that the $Cr(en)_3^{3+}$-attapulgite would not be useful for application as a GSC packing material.

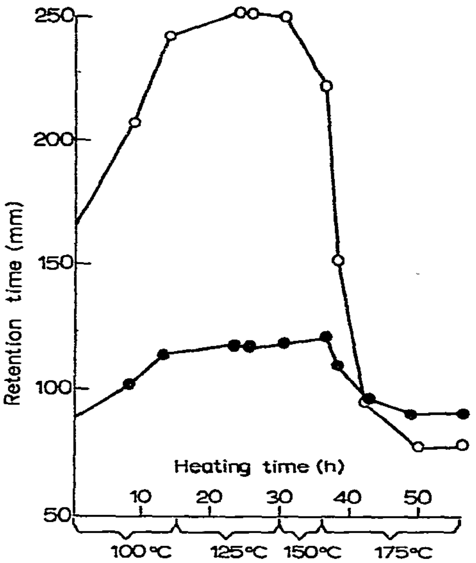

Fig. 2. Retention time *versus* heating time of (○) N_2O at 50° and 120 ml/min, and (●) C_2H_6 at 50° and 120 ml/min obtained on a 110-cm column of 100% $Cr(en)_3^{3+}$-hectorite.

The results thus far would indicate that either $Cr(en)_3^{3+}$-montmorillonite or $Cr(en)_3^{3+}$-hectorite could be used satisfactorily as GSC packing materials for separation of light hydrocarbons.

A further study of substitution onto other types of clays is presently being pursued.

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